Unexpected ligand substitutions in the cluster core $\{Re_6Se_8\}$: synthesis and structure of the novel cluster compound $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3\cdot 4H_2O$†

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The compound $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3\cdot 4H_2O$ containing a novel cluster core $\{Re_6Se_4O_4\}$ with ordered ligands, where the 4 positions of one face of a Se_4O_4 cube are occupied exclusively by Se atoms and 4 O atoms lie in the opposite face was synthesized *via* the interaction of solid $Re_6Se_8Br_2$ with molten KOH.

The chemistry of octahedral rhenium(III) cluster compounds with an $[Re_6Q_8]^{2+}$ cluster core (Q = S, Se, Te) is in a stage of rapid development.[1] The series $Re_6Q_8X_2$ (Q = S, Se; X = Cl, Br)[2] is representative of similar compounds where inter-cluster bonding is very extensive. A large number of articles have appeared within the last few years that have reported the preparation of molecular cluster complexes of the type $Re_6Q_8L_6$ (L = Cl, Br, I, CN or different organic ligands).[3] The outer ligands L in complexes $Re_6Q_8L_6$ can easily be substituted whereas the inner ligands Q are rather inert. Only a few examples are known for the substitution of one or two μ_3-ligands by oxygen in the cluster core of octahedral rhenium chalcohalide complexes: $\{Re_6S_5OCl_2\}^{2+}$,[4] $\{Re_6Se_4O_2Cl_2\}^{4+}$[5] and $\{Re_6S_6O_2\}^{2+}$.[6]

In this paper we present a new route for the chemical modification of octahedral rhenium cluster complexes and the preparation of the novel compound $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3\cdot 4H_2O$ containing a cluster core with unusual composition and structure $\{Re_6Se_4O_4\}$. This oxyselenide rhenium cluster compound was synthesized using the interaction of solid $Re_6Se_8Br_2$ with molten KOH at 280 °C in an open vessel. $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3\cdot 4H_2O$ has been isolated from an aqueous solution of the reaction products by adding HCl + CsCl and evaporating.‡ During the reaction of $Re_6Se_8Br_2$ with molten KOH, the cluster core $\{Re_6Se_8\}$ undergoes an unexpected transformation into a new cluster core $\{Re_6Se_4O_4\}$. The title compound is the first example of a substitution of four μ_3-Se ligands by four μ_3-O ligands in a cluster with an octahedral core; moreover the Se and O ligands are ordered: they lie in opposite faces of the Se_4O_4 cube.

The main building unit of the structure is the cluster anion $[Re_6Se_4O_4Cl_6]^{4-}$ (Fig. 1).§ The irregular shape of the anion (point symmetry C_1) is caused by substantial differences in the nature and arrangement of the μ_3-ligands (oxygen and selenium). In the distorted cube $(\mu_3\text{–}Se)_4(\mu_3\text{–}O)_4$, 4 Se atoms form one face opposite to a face formed by 4 O atoms. Oxygen atoms are grouped around Re(1), whereas Se atoms surround Re(6). The terminal bonds Re–Cl are nearly perpendicular to the faces so that the Re–Cl bonds are somewhat inclined towards Re(6). The non-equivalence of the μ_3-ligands results in a considerable variation of Re–Re distances, where the shortest bonds (2.4612(9)–2.4625(9) Å) include Re(1), and the longest ones (2.6105(9)–2.6178(9) Å) are observed for Re(6). The bond lengths Re–Se, 2.5108(18)–2.5574(19) Å, Re–Cl, 2.359(4)–2.431(5) Å, and Re–O, 2.076(11)–2.179(10) Å, are comparable with known values[4–6] from analogous compounds.

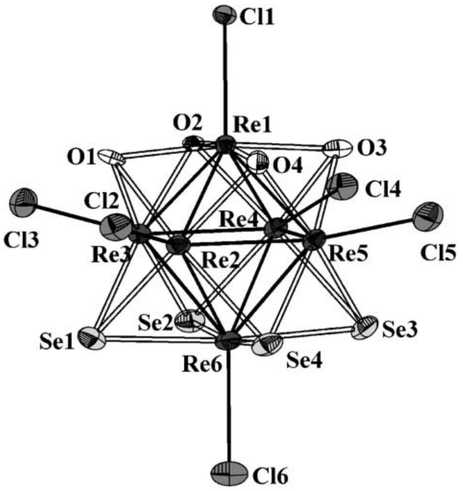

Fig. 1 Structure of cluster anion $[Re_6Se_4O_4Cl_6]^{4-}$.

In the crystal structure, the cluster anions and caesium atoms arrange in double layers parallel to (001) and the rhombohedral cell comprises three such layers. The fragment of packing of cluster complexes $[Re_6Se_4O_4Cl_6]^{4-}$ is shown in Fig. 2. Cs1 atoms are located in channels formed by Cl1 and Cl2 atoms; μ_3–O ligands lie towards the inside of the channel. The Cs1, Cs4 and O2W atoms lie on three-fold axes.†

In the IR spectrum of the compound there are three absorption bands at 433, 620 and 650 cm^{-1} which can be assigned to Re–O vibrations.

To confirm the presence of acidic protons, a solid-state NMR investigation has been carried out. The wide-line ^1H NMR spectra were recorded as a first derivative of the NMR absorption line by sweeping the frequency in the neighborhood of 25 MHz using a

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† Electronic supplementary information (ESI) available: figs. of unit cell in two projections, schematic HOMO and LUMO for C_{4v} $Re_6O_4Se_4Cl_6$. See http://www.rsc.org/suppdata/cc/b4/b412850h/

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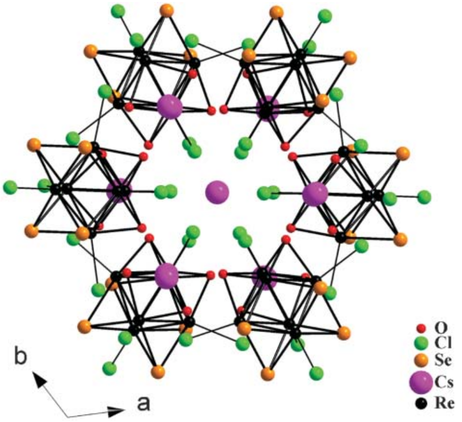

Fig. 2 Fragment of the packing along the *c* axis.

Table 1 The bond energies calculated for the isomers $[Re_6Se_4O_4Cl_6]^{4-}$ with different symmetry, *E* (eV)

I (C_{4v})	**II** (T_d)	**III** (C_s)	**IV** (D_{2h})	**V** (C_2)	**VI** (C_{3v})
−125.54	−124.45	−125.05	−125.12	−125.32	−125.25

home-made NMR spectrometer with signal accumulation. A small-volume powder sample (mass ≈0.1 g) was used. The hydrogen content obtained from the NMR integral intensity measurements was 11.3(6), in reasonable agreement with the value expected from the X-ray data. In the temperature range of 190 to 330 K, the NMR spectrum appears as a narrow Lorentzian-shaped line (Fig. 3) indicating a fast mobility of the hydrogen atoms, which results in practically total suppression of the magnetic dipole–dipole interactions of protons. From the temperature dependence of the line half-width (the inset in Fig. 3), the activation energy of the hydrogen motion was estimated as 13(1) kJ mol^{-1}. This low-energy hydrogen migration cannot be associated with the H_2O self-diffusion only, since in hydrated rhenium cluster compounds through their low symmetry, the diffusion-induced suppression of the strong intramolecular interaction of protons is incomplete. That usually brings about rather wide spectra with a specific fine structure.[7] Most likely, in the crystal studied, the H_2O diffusion is accompanied by the intense intermolecular proton exchange resulting from the proton-transfer reactions between H_2O molecules and acidic sites and leads to effective averaging of all dipole–dipole interactions. We suppose that the protonation of one of the water molecules with formation of the stable H_3O^+ ion takes place. However, the possibility of the acidic proton's location in the vicinity of one of electronegative atoms of the rhenium cluster must not be ruled out. We hope to elucidate this alternative from the low-temperature NMR measurements which are in progress.

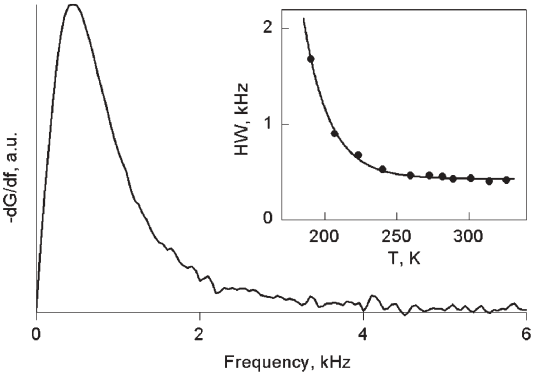

Fig. 3 Experimental ^{1}H NMR absorption derivative at 290 K. Inset: the temperature dependence of the line half-width.

In general, the complex $[Re_6Se_4O_4Cl_6]^{4-}$ may exist in the form of six isomers of different symmetry in which the selenium atoms can occupy the positions as follows: 1,2,3,4 (**I** - C_{4v}); 1,3,2′,4′ (**II** - T_d); 1,2,4,3′ (**III** - C_s); 2,4,2′,4′ (**IV** - D_{2h}); 1,2,4,2′ (**V** - C_2) and 1,2,4,1′ (**VI** - C_{3v}) (the numbers with primes indicate the oxygen atom positions in Fig. 1). The different possible $[Re_6Se_4O_4Cl_6]^{4-}$ isomers have been examined by calculations within density functional theory (DFT). The calculations of bond energies give the result that all isomers are possible, but the **I** (C_{4v}) is the most stable (Table 1). The result is in good agreement with the experimental data. The calculated charge distribution suggests that this complex could be formulated as $Re(5)^{0.05}Re(4)^{0.23}$-$Re_4{}^{0.14}Se_4{}^{-0.22}O_4{}^{-0.28}Cl(5)^{-0.48}Cl(4)^{-0.47}Cl_4{}^{-0.48}$. The small charge values indicate the preferentially covalent character of the interactions in the $[Re_6Se_4O_4Cl_6]^{4-}$ complex. It is interesting to note that the Re(5)–Cl(5) bond is the least polarized in comparison with other Re–Cl bonds.

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Notes and references

‡ $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3{\cdot}4H_2O$ was synthesized by heating a mixture of 1 g $Re_6Se_8Br_2$ and 1.5 g KOH at 280 °C for 30 minutes in a carbon glass vessel in air. After cooling, the resulting melt was washed with i-PrOH (3 × 20 mL portion) and dissolved in 60 mL water and filtered. CsCl (1.5 g) and HCl (10 mL) were added to the solution that was then boiled for 1.5 h. The solution was filtered, evaporated to 20 mL and cooled. After 12 hours, red crystals were filtered off, washed with 10 mL cold water and air-dried. Yield: 0.45 g (38.5%). EMA: $Cs_{3.7}Re_6Se_{3.7}Cl_{6.3}$. *Structure Determination.* Single-crystal X-ray diffraction data were collected on a Bruker Nonius X8Apex diffractometer equipped with a 4 K CCD area detector. SHELX-97 program set for structure solution (direct methods) and refinement (full-matrix least-squares on F^2).[8] CCDC 249409. See http://www.rsc.org/suppdata/cc/b4/b412850h/ for crystallographic data in .cif or other electronic format.

§ Crystal data: $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3{\cdot}4H_2O$, M_r = 6682.32, trigonal, $R\bar{3}$, a = 17.1360(3), c = 47.4916(14) Å, V = 12077.2(5) Å^3, Z = 6, $\rho_{calc.}$ = 5.513 g cm^{-3}, μ = 37.889 mm^{-1}, T = 293(2) K. Reflections: 9389 collected, 5048 unique (R_{int} = 0.0322), 3450 observed [$I > 2\sigma(I)$]; 244 parameters refined with $R1$ = 0.0416, $wR2$ = 0.1088, $\Delta\rho_{min/max}$ = +3.073, −2.450 e Å^{-3}. CSD–391281. The DFT calculations were carried out using the ADF2002 program.[9] The local-exchange correlation potential was used for the local density approximation, Becke's non-local corrections to the exchange energy and Perdew's non-local corrections to the correlation energy were added. The triple-ζ STO basic set without core-potentials was used for all atoms. The ZORA method was used to account for the scalar relativistic effects. The electronic structure calculations were carried out for

$[Re_6O_4Se_4Cl_6]^{4-}$ models with full optimizations. The calculations of the electronic binding energy have been performed for the reaction $6Re + 4Se + 4O + 6Cl + 4e^- \rightarrow [Re_6Se_4O_4Cl_6]^{4-}$. The atomic net charges for several $[Re_6Se_4O_4Cl_6]^{4-}$ clusters were obtained using the Hirshfeld analysis.[10]

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